12 1E

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) 14 NRL-MR-4609

9 **REPORT DOCUMENTATION PAGE** — READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: NRL Memorandum Report 4609	2. GOVT ACCESSION NO.: AD-A103266
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle): 6 THE SOLUBILITY OF WATER IN CURRENT JP-5 JET TURBINE FUELS	5. TYPE OF REPORT & PERIOD COVERED: Interim report on one phase of an NRL problem.
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): 10 W. A. Affens, R. N. Hazlett, [redacted] J. D. DeGuzman	8. CONTRACT OR GRANT NUMBER(s): 17
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Naval Research Laboratory, Washington, DC 20375	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 62765N; ZE65571006; 61-0085-0-1
11. CONTROLLING OFFICE NAME AND ADDRESS: Naval Air Propulsion Center, Trenton, NJ 08628 (11) 25	12. REPORT DATE: Aug[redacted]81
	13. NUMBER OF PAGES: 14
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): 16 ZE65571	15. SECURITY CLASS. (of this report): UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

DTIC

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Jet fuels	Water solubility
JP-5	Aromatics
Hydrocarbons	Shale-II

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Current JP-5 jet fuels have been observed to contain significantly greater concentrations of aromatic hydrocarbons than had been reported for earlier JP-5 samples. Water solubility is a very important property of jet fuels and is greatly influenced by aromatic concentration. For these reasons, a study was made of current JP-5 fuel samples to determine whether they might exhibit a greater water solubility than that of earlier JP-5

(Continues)

DD FORM 1473, 1 JAN 73 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

251950

20. ABSTRACT (Continued)

fuels. Water solubility measurements of ten relatively recent JP-5 fuel samples were determined at 10°, 25°, and 40° C.

The water solubilities, on the average, were about 25% greater than that from earlier literature data. This suggests that the increased aromatic content plays a part in the increased water solubility.

The water solubilities were found to vary with temperature in accordance with the Van 't Hoff equation as is normal with hydrocarbon mixtures. The straight line plots of the logarithm of concentration vs. reciprocal temperature gave typical slopes and intercepts.

CONTENTS

THE SOLUBILITY OF WATER IN CURRENT JP-5 JET TURBINE FUELS

INTRODUCTION

Hydrocarbon fuels contain water under typical usage conditions. This is particularly true of Navy fuels which are frequently in contact with sea water. The water in fuel consists of dissolved water and free water (1-4). Water in jet fuels can be a serious hazard since it can freeze out in the fuel system and result in mechanical difficulties in the engine, fuel lines, filters and in other locations of the aircraft (3). In addition, free water is a critical contaminant in jet fuels because it plays a major role in corrosion and in microbiological growth. For these reasons free water is usually removed by a filter separator (1). Dissolved water, however, may also be a problem because it can become free water as water-saturated fuel is cooled.

The amount of water which can dissolve in a given fuel depends on fuel composition and temperature (3-6). Water is much more soluble in aromatic and olefin compounds than in saturated hydrocarbons (6). Since 1953 there appears to have been a slight upward trend in the aromatic content of JP-5 jet fuels (7,8), and current samples show a relatively large increase. For this reason it was decided to compare the water solubility of relatively recent JP-5 fuels with that previously reported in the literature (3, 5, 9) to determine whether the increasing aromatic content would make a difference.

SOLUBILITY OF WATER IN HYDROCARBONS AND FUELS

There are considerable literature data on the solubility of water in hydrocarbons at various temperatures. Water solubility data have been reported in petroleum fractions (5, 9, 10), jet and ship fuels (3, 5, 9), and in pure individual hydrocarbons (5, 9-12). The solubility of water in hydrocarbons is not high for typical distillate fuels, varying from about 35 to 400 ppm by weight depending on the fuel composition and temperature (3, 5, 9,). For pure normal alkanes, ranging down from hexadecane to heptane, Schatzberg (11) found the water solubility to vary from 91 to 54 ppm by weight at 25°C and from 136 to 104 ppm at 40°C. Zimmerman (5) found that water was considerably more soluble in benzene (using sea water). For example at 25°C, the solubility in benzene, about 750 ppm by weight, was about ten times that of the average values for the n-alkanes at that temperature.

AROMATIC AND OLEFINIC CONTENT OF JP-5 JET FUELS

The maximum amounts of aromatics and olefins permitted in JP-5 by its military specification requirements (13) are 25% and 5% by volume respectively. From Bureau of Mines (7) and Department of Energy (8) surveys, as shown in Table I, the olefin content has averaged about 1.3% by volume since 1953, and has shown signs of decreasing slightly. In any case, the olefin content has been considerably below the 5% maximum permitted. Although water is more soluble in olefins than in aromatic hydrocarbons (5, 6, 12), because of the higher concentrations of the latter in JP-5 fuels (4), the aromatics would be expected to exert a greater influence on the water solubility in JP-5. As seen in Table I, the aromatic content shows a slight increase with time.

Manuscript submitted July 16, 1981.

JP-5 JET FUEL SAMPLES

Ten representative current production JP-5 samples from nine different domestic refineries were studied. In addition, a single shale derived sample (14) was studied. For comparison, two pure (99 mole%) *n*-alkanes were also investigated, *n*-undecane and *n*-dodecane. All the JP-5 fuels had been reported to have met the specification requirements (13). The aromatic and olefin contents of eight of these samples are shown in Table II. The data (except for J-22A) are from available Navy inspection reports. The olefin content data are similar to the data in Table I, but the aromatic content data are considerably higher than that reported in the earlier surveys. The average aromatic content is 21.8% (for seven of the petroleum derived fuels) which is considerably above the average in the survey data.

EXPERIMENTAL

(a) Water Saturation of Fuels - The fuels were saturated with water by the static water saturation method used by both Schatzberg (11) and Zimmerman (5). The fuels were treated by storing them over a layer of distilled water in 4-oz glass serum bottles with tightly sealed serum caps. The bottles and samples were submerged in a constant temperature bath (± 0.02°C) for each of three separate runs at 10°, 25° and 40°C. The samples were kept in the bath without agitation for seven to ten days. This period had been found to be sufficient by Schatzberg to attain complete water saturation (11).

(b) Sampling - Twenty-ml samples were taken by means of a 20.0-ml hyperdermic syringe and needle. Dry nitrogen pressure applied by means of a second needle through the stopper was used to reduce sampling time. The technique is the same as used by Zimmerman (5), but nitrogen pressure was used instead of air. The syringe and needles were precoated internally with a silicone fluid to prevent loss of dissolved water from the fuel sample to the surfaces of the syringe and needle.

(c) Water Determination - The water was determined by means of Karl Fischer titration method similar to that of the ASTM D-1744 procedure (15). The samples were titrated automatically to an electrometric end point. Water concentrations were converted to parts per million by weight using average densities (13, 17) for the JP-5 samples and literature values (18) for the two pure *n*-alkanes.

RESULTS

Results are shown in Table III. The experimental water solubility data (C, ppm w/w) at 10°, 25° and 40°C are shown on the left in the table. Averages of the results of two of the three individual determinations are shown in the table. The average deviations between individual determinations and their averages varied from ±0.2% to ±5.4% with an overall average deviation of ±2.2%. Data for each sample were plotted on a standard semi-logarithm plot ($\ln C$ vs $1/T$). Since all the data fell in a relatively narrow range, it was not feasible to place all the data on a single plot. The data for three selected samples are shown in Figure 1. Sample No. 80-5 represents a relatively high water solubility fuel; 80-14 a low solubility one; and 80-10 a fuel which was close to the average of the

Table I - Average literature survey data of aromatic and olefin content of JP-5 fuels (4,7,8)

Survey Period	Aromatics (% v/v)	Olefins (% v/v)
1953 - 1960	10.1	1.9
1961 - 1970	15.1	1.4
1971 - 1980	16.1	0.9

Table II - Aromatic and Olefin Content of JP-5 Fuel Samples (Navy Turbine Fuel Test Inspection Reports)

NRL No.	Aromatics (% v/v)	Olefins (% v/v)
Military Spec. MIL-T-5624L (Max.) (13)	25.0	5.0
80-5	23.9	1.5
80-6	22.1	0.5
80-7	22.6	0.9
80-10	23.4	0.1
80-11	21.8	1.9
80-12	20.0	1.3
80-14	19.0	0.5
Average	21.8	1.0
J-22A*	24.0	1.6

* - JP-5 from Shale-II program (14); data by private communication from Naval Air Propulsion Center

Table III - Solubility of Water in Jet Fuel Samples at Three Temperatures
— Concentration (C, ppm w/w) vs. Temperature (C°) —

NRL No.	Experimental Data 10°	25°	40°	Slope* -m	Intercept* b	Averaged Data* 10°	25°	40°
80-5	60	101	172	3110	15.07	60	105	172
80-6	50	96	162	3478	16.21	51	95	166
80-7	50	92	176	3714	17.01	50	97	175
80-8	44	91	167	3945	17.72	45	96	171
80-9	57	86	167	3162	15.16	55	98	160
80-10	54	97	164	3284	15.59	54	98	166
80-11	58	96	175	3256	15.34	57	102	172
80-12	57	105	171	3250	15.53	60	104	175
80-13	50	107	172	3663	16.88	52	101	181
80-14	53	90	147	3014	14.62	53	92	148
Average	53	96	167	3388	15.93	53	98	168
Minimum	44	86	147	3945	17.72	45	91	148
Maximum	60	107	176	3014	14.62	60	105	181
J-22A**	49	99	170	3682	16.91	50	97	175
n-$C_{11}H_{24}$	33	66	115	3694	16.55	34	65	118
n-$C_{12}H_{26}$	33	65	109	3536	16.00	34	64	112

* - Calculated by Linear Regression Treatment, where $\ln C = m/T\ °K + b$.

** - JP-5 from Shale-II program (14).

ten JP-5 fuels. Data for n-undecane, n-dodecane and the Shale-II JP-5 (J-22A) are plotted along with the average data for the ten petroleum fuels in Figure 2.

It was found in almost all cases that the data fell on straight lines. The slopes (m) and intercepts (b) for these lines are shown in the table. The slope and intercept data were calculated by a linear regression treatment, as were the "average data" on the right side of Table III. The average deviation between the experimental values and the linear regression data ("Averaged Data" in Table III) is about $\pm 3\%$. The straight lines plotted in Figures 1 and 2 represent data obtained by linear regression, where $\ln C = m/T\ °K + b$.

OBSERVATIONS

Several observations may be made from the data in Table III, and Figures 1 and 2:

(a) The solubility of water in JP-5 fuels increases with temperature in accordance with the Van't Hoff equation (5, 12) yielding a linear plot when ln C is plotted against 1/T °K.

(b) The data for the ten JP-5 fuels in this series of tests fall into a relatively narrow range.

(c) The slopes of these graphs are negative, and both the slopes and intercepts show considerable variation between samples.

(d) The data for the Shale-II JP-5 (J-22A) match that of the average data for the ten petroleum JP-5 fuels.

(e) The water solubility in the two alkanes is less than that in the JP-5 fuels, but the alkane slopes and intercepts are within the range of the ten JP-5 samples.

(f) The water solubility in n-undecane is only slightly greater than that of n-dodecane.

(g) The water solubilities in the two pure alkanes at 25° and 40°C agree within experimental error with Schatzberg's data (11).

COMPARISON OF NRL DATA WITH OLDER LITERATURE DATA

Figure 3 shows a comparison of this data with that of older literature data (3, 5, 9) for water solubility vs. temperature. Two envelopes of data shown in the graph represent maximum and minimum ranges for both sets of values. It can be seen that the current data are higher than that of the older data. The average (median) value of the current data is approximately the upper limit of the older solubility range. The median value of the current fuels shows an approximately 25% average increase over that on the median of the older data. The greater solubility of water in the current JP-5 fuels appears to be consistent with their increased aromatic content.

SUMMARY AND CONCLUSIONS

A study has been made concerning the water solubility vs. temperature for current representative JP-5 fuels for comparison with that of older literature data. This study was made because it was believed that the higher aromatics content of current JP-5 fuels might result in higher water solubility. Water determinations were made by the Karl Fischer method on fuel samples which had been saturated with water at 10°, 25° and 40°C. The water solubility in current JP-5 fuels was found to increase with temperature in accordance with the Van't Hoff equation in the same manner as in pure hydrocarbons and other fuels. Slopes (m) and intercepts (b) of the lines formed in plots of Ln C vs. 1/T graphs were used to obtain averaged data for comparisons. The higher water solubility in current JP-5 fuels appears to be consistent with its higher aromatic content.

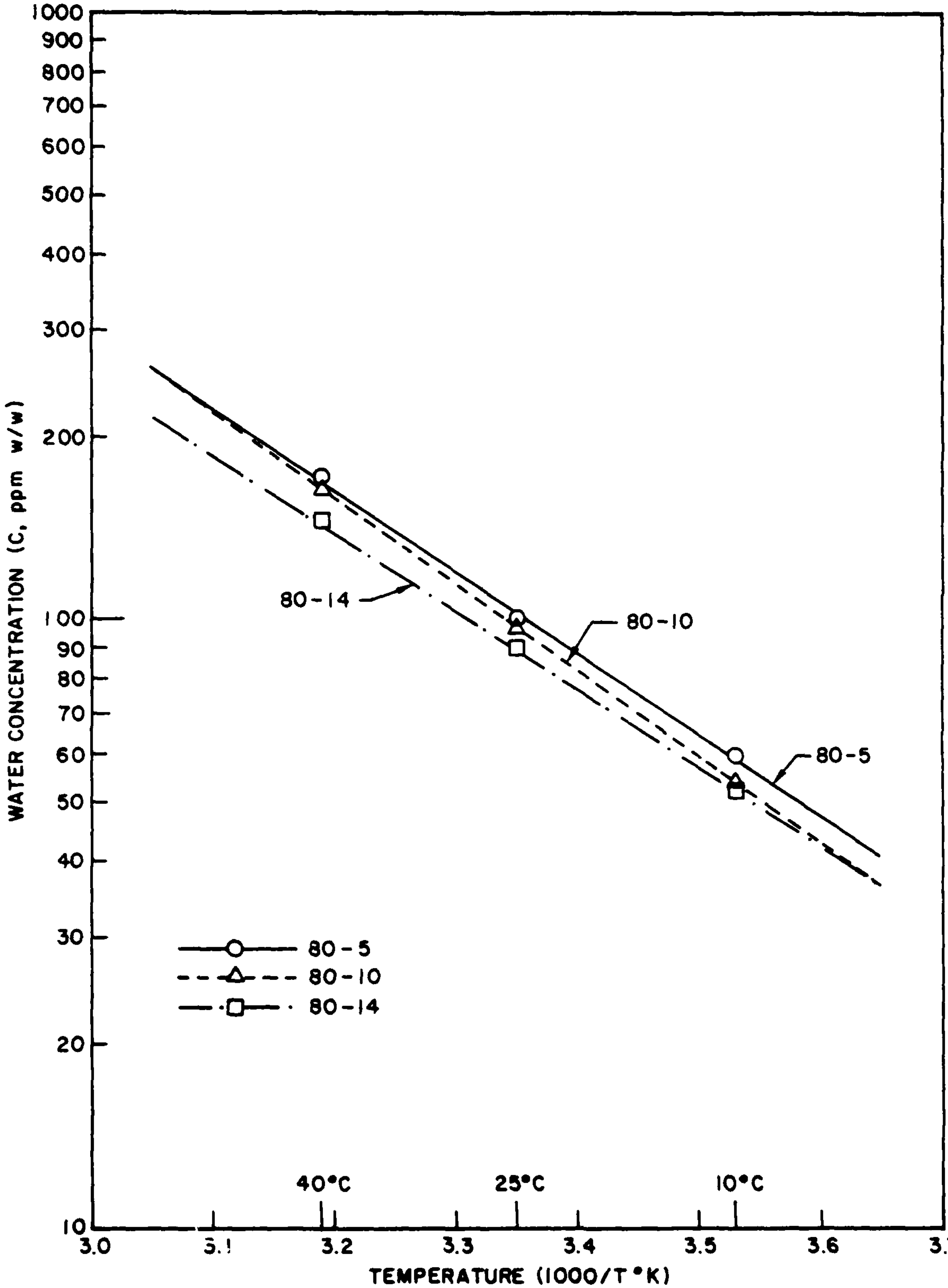

Fig. 1 — Water concentration vs. temperature — JP-5 fuels

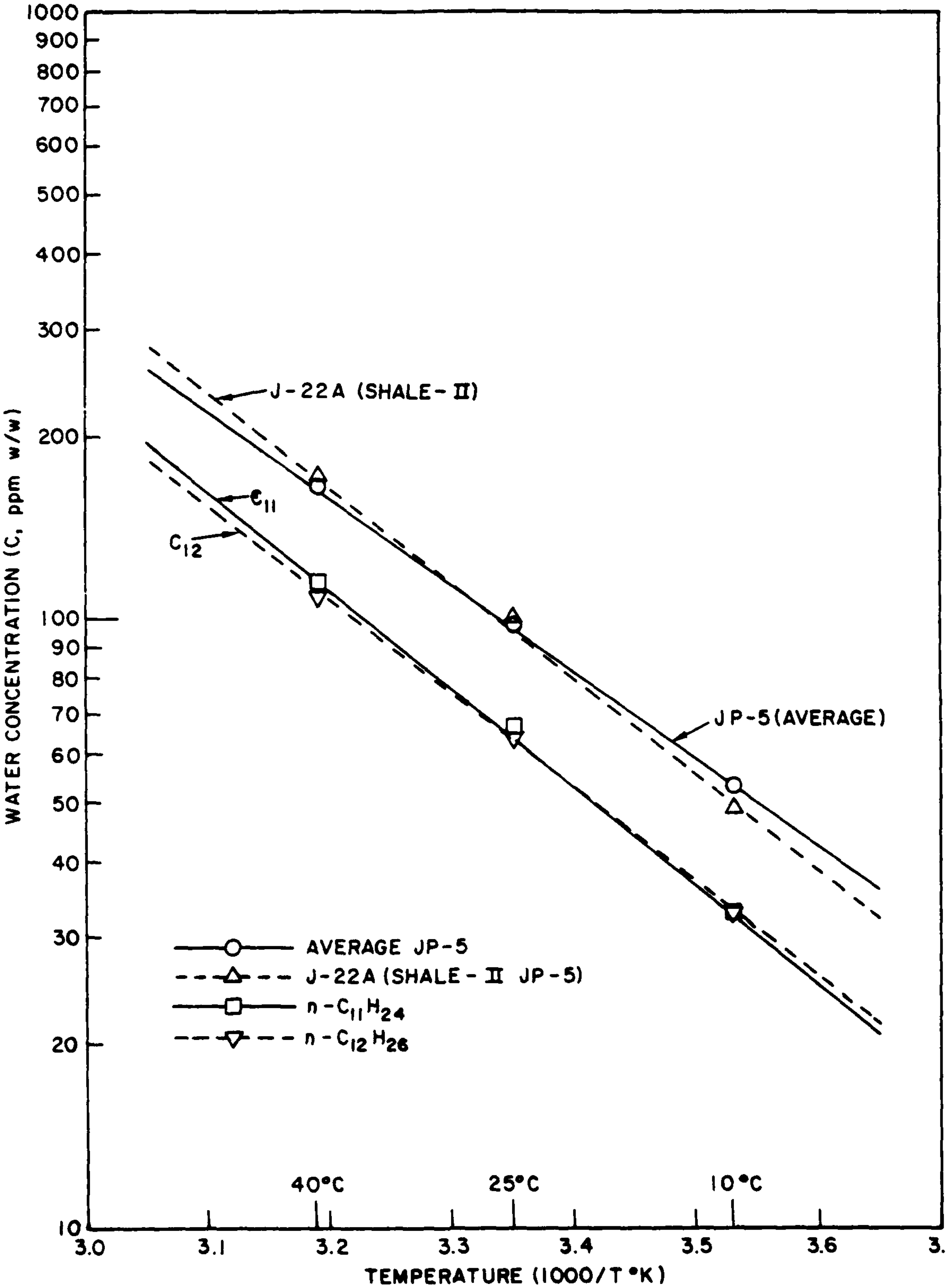

Fig. 2 — Water concentration vs. temperature — JP-5 fuels, n-C_{11} and n-C_{12}

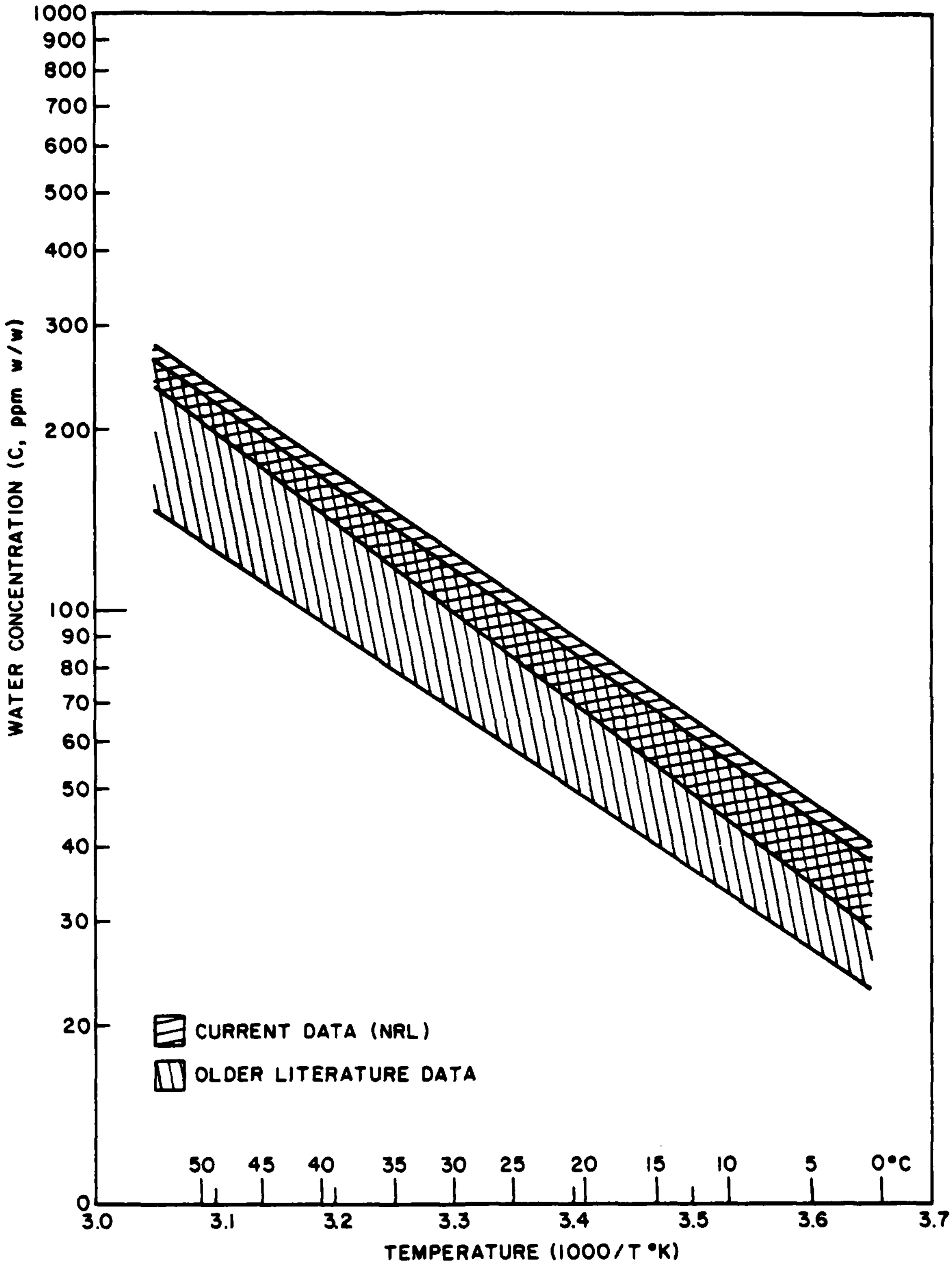

Fig. 3 — Solubility of water in JP-5 fuels — current data vs. older literature data (3, 5, 9)

REFERENCES

(1) R. N. Hazlett and H. W. Carhart, "Removal of Water from Fuel Using a Fibrous Bed", Filtration and Separation, 9, 456, July/August 1972.

(2) J. A. Krynitsky, "The Problem of Jet Fuel Contamination", Naval Research Reviews, February 1964, 13-18.

(3) J. D. Rogers, J. A. Krynisky and A. V. Churchill, "Jet Fuel Contamination: Water, Surfactants, Dirt, and Microbes", SAE Natl. Aerospace Engr. and Mfr. Meeting, Los Angeles, October 1962, Reprint 583C.

(4) H. C. Barnett and R. R. Hibbard, "Properties of Aircraft Fuels", NACA Technical Note 3276, August 1956.

(5) John G. Zimmerman, "The Solubility of Water in Navy Distillate Fuels and Hydrocarbons in Contact with Synthetic Sea Water at Temperatures of 50° to 120°F". NSRDC Report 4165, October 1973.

(6) Kozo Shinoda, "Principles of Solution and Solubility", Marcel Dekker, New York 1978.

(7) C. M. McKinney, O. C. Blade and E. M. Shelton, "Aviation Fuels, 1969", Petroleum Products Survey No. 64, March 1970, Bureau of Mines.

(8) E. M. Shelton, "Aviation Turbine Fuels, 1980", Petroleum Products Survey No. 119, March 1981, Dept. of Energy.

(9) W. D. Garrett and J. A. Krynitsky, "Determination of Water in Jet Fuels and Hydrocarbons", NRL Report 4997, Sept. 4, 1957.

(10) J. Griswold and J. E. Kasch, "Hydrocarbon-Water Solubilities at Elevated Temperatures and Pressures", Ind. Engr. Chem. 34, 804 (1942).

(11) P. Schatzberg, "Solubilities of Water in Several Straight-Chain Hydrocarbon Liquids from C_7 to C_{16}", NSRDC Report 2586, Jan. 1968.

(12) C. Black, G. Joris and H. S. Taylor, "The Solubility of Water in Hydrocarbons", J. Chem. Phys. 16, 537 (1948).

(13) "Military Specification, Tubine Fuel, Aviation Grade, JP-4 and JP-5", MIL-T-5624L, 18 May 1979.

(14) N. J. Wasilk and E. T. Robinson, "The Commercial Scale Refining of Paraho Crude Shale Oil into Military Specification Fuels", Preprints, Division of Fuel Chem., ACS, 25, August 24-29, 1980.

(15) American Society for Testing and Materials, "Standard Test Method for Water in Liquid Petroleum Products by Karl Fischer Reagent", ASTM D 1744-64, 1964.

(16) American Society for Testing and Materials-The Institute of Petroleum," ASTM-IP Petroleum Measurement Tables", Amer. Edition, ASTM D-1250, 1952.

(17) W. A. Affens, "Shipboard Safety, A Meaningful Flash Point Requirement for Navy Fuels", NRL Report 7999, October 28, 1976.

(18) R. R. Dreisbach, "Physical Properties of Chemical Compounds-II", Advances in Chemistry Series No. 22, American Chemical Society, Washington, D. C. 1959.